

High-Nitrogen-Based Pyrotechnics: Longer- and Brighter-Burning, Perchlorate-Free, Red-Light Illuminants for Military and Civilian Applications

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Dedicated to United States Marine 2nd Lieutenant John T. Wroblewski for his bravery, valor, and selfless service.

Abstract: The full-up prototype testing of perchlorate-free, hand-held, signal illuminants for the US Army's M126A1 red star parachute hand-held signal is described. Compared to the perchlorate-containing control, the disclosed illuminants yielded excellent stabilities toward various ignition stimuli while offering superior pyrotechnic perfor-

mance. Militarily, the illuminants provided further evidence that development of smaller hand-held signal items in an environmentally conscious way is

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a realistic and obtainable goal. The results are also important from the perspective of civilian fireworks, as the development of brighter, longer-burning, and environmentally compatible red-light-emitting pyrotechnics is now possible.

Introduction

Over the past several years, there has been an interest in the development of environmentally friendly pyrotechnics for military and civilian applications.^[1] In particular, the removal of heavy metals, such as barium, from green-light-emitting pyrotechnics and the removal of perchlorate oxidizers from many colored pyrotechnic formulations lies at the forefront of this research area. Barium compounds, long associated with green-light emission, are believed to be human-health and environmental hazards.^[2] Armament research, development and engineering center (ARDEC) recently developed barium-free green-light emitters with acceptable burn times for pyrotechnic applications by using potassium nitrate–amorphous boron–crystalline boron/boron carbide–epoxy

binder mixtures.^[3,4] Moreover, it was discovered by ARDEC that a potassium nitrate–boron carbide–epoxy binder mixture alone was able to generate suitable green-light emission.^[4]

Potassium perchlorate and ammonium perchlorate oxidizers, once believed to be amongst the ideal oxidizers due to their inherent reactivity, stability, low cost, low hygroscopicity, and large positive oxygen balances, have now been identified as an environmental and human-health hazard.^[5] Perchlorates have high water solubilities and are suspected groundwater contaminants, thus posing a potential risk to drinking supplies. Perchlorates are believed to be teratogenic, and the anion competes with iodide anions in binding with the thyroid gland, interfering with production and regulation of thyroid hormones. This binding effect, according to Conkling and Mocella, appears to be reversible, as the intake of iodide-containing food and beverages appears to lead to the replacement of perchlorate anions with iodide anions.^[6] Nonetheless, the US environmental protection agency has set the federal permissible perchlorate limit in groundwater to 15 ppb,^[7] whereas the states of California and Massachusetts have set their respective permissible levels to 6 ppb and 2 ppb.^[8]

Because of these low permissible levels, US military personnel have not been allowed to effectively train with perchlorate-containing munitions on training ranges within and outside the continental USA. The inability to properly train for combat operations endangers military readiness and thus decreases survivability on the battlefield.

The civilian fireworks industry is also coming under increasing scrutiny by environmental groups and the EPA to “green” their fireworks, and to develop perchlorate-free var-

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| 14. ABSTRACT The full-up prototype testing of perchlorate-free, hand-held, signal illuminants for the US Armys M126A1 red star parachute hand-held signal is described. Compared to the perchlorate-containing control, the disclosed illuminants yielded excellent stabilities toward various ignition stimuli while offering superior pyrotechnic performance. Militarily, the illuminants provided further evidence that development of smaller hand-held signal items in an environmentally conscious way is a realistic and obtainable goal. The results are also important from the perspective of civilian fireworks, as the development of brighter, longer-burning, and environmentally compatible red light-emitting pyrotechnics is now possible. | | | | | |
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itants. The manufacturing of fireworks is believed to lead to significant perchlorate contamination in soil and groundwater, and significant levels of perchlorates have been found in the environment after firework displays.^[9]

The use of high-nitrogen energetic salts for pyrotechnic applications as perchlorate replacements has been the subject of intense investigation in recent years and the synthesis, characterization, and remarkable stabilities of the high-nitrogen salts have been demonstrated previously by Klapötke, Damavarapu, and co-workers.^[1a,10] Rather than deriving the combustion energies from the oxidation of a carbon backbone, high-nitrogen compounds derive the energy from high heats of formation, attributed to the substantial amount of environmentally benign nitrogen gas (N₂) released upon combustion of these materials.

To address the aforementioned perchlorate issues, an effort was initiated by ARDEC to remove potassium perchlorate from their red-light-emitting pyrotechnic items—the M126A1 red star parachute hand-held signal (HHS). HHSs are used in training and combat situations for the purposes of signaling military and allied personnel and aircrafts. Although Klapötke and ARDEC were recently successful in developing perchlorate-free M126A1 red-light-emitting formulations on a small scale,^[11,12] successful formulation development at the prototype level (i.e., production scale) with high-nitrogen compounds had never been done. Because substantial differences in pyrotechnic performance can arise as one moves from small-scale testing to prototype testing, it is imperative that formulations be proven out at the prototype level because these tests are indicative of how a formulation will behave when produced and put into a military item. Although ARDEC's primary focus lies in the area of military pyrotechnics, development of perchlorate-free, red-light-emitting illuminants would also have a positive impact on the civil fireworks community.

Results and Discussion

The US Army in-service M126A1 perchlorate-containing control is provided in Table 1. Because potassium perchlorate is an energetic oxidizer and decomposes in an exothermic process,^[6] to remove it from the formulation means that energy is removed from the pyrotechnic system. As described and demonstrated previously,^[11,12] strontium bis(1-methyl-5-nitriminotetrazolate) monohydrate (**1**, Figure 1), was selected to replace potassium perchlorate because of the high-energy nature, stability toward various ignition

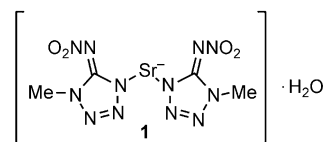


Figure 1. Strontium bis(1-methyl-5-nitriminotetrazolate) monohydrate.

stimuli, and because of the potential to contribute to red-light emission.

Formulations **A** and **B** were developed on a small scale,^[12] and their compositions are summarized in Table 2. Compared to the control, formulations **A** and **B** are free of perchlorate, contain a single magnesium mesh size instead of

Table 2. Perchlorate-free formulations **A** and **B**.

| Components | Formulation A [Wt %] | Formulation B [Wt %] |
|-----------------------|-----------------------------|-----------------------------|
| strontium nitrate | 39.3 | 39.3 |
| magnesium 30/50 | 29.4 | 35.4 |
| PVC | 14.7 | 14.7 |
| 1 | 9.8 | 3.8 |
| Epon 813/Versamid 140 | 6.8 | 6.8 |

two, and contain an epoxy-based instead of a polyester-based binder system. The replacement of the Laminac binder system is of importance because this material contains styrene monomers, a suspected carcinogen and volatile organic compound (VOC), which presents a fire/explosion hazard during the production process of HHS items. The Laminac binder system has a short shelf life of about six months before decomposing, and it is also plagued by single-point-of-failure concerns.^[13] Therefore, replacement of Laminac binder systems with a widely available binder system, such as Epon 813/Versamid 140, would ensure the future viability and producibility of the M126A1 HHS for US military personnel.

The small-scale performance of formulations **A** and **B** against the control, as discussed previously, is provided in Table 3.^[12] Because formulations **A** and **B** exceeded the performance of the control in burn time, luminous intensity, and spectral purity, and had comparable dominant wavelengths, these formulations were evaluated at the prototype level on the scale encountered during production of M126A1 munitions.

Gratifyingly, the performances of illuminant formulations **A** and **B** at the prototype level easily exceeded the military requirements established by the US military across the

Table 1. M126A1 control formulation.

| Components | [Wt %] |
|-----------------------|--------|
| strontium nitrate | 39.3 |
| magnesium 30/50 | 14.7 |
| magnesium 50/100 | 14.7 |
| polyvinyl chloride | 14.7 |
| potassium perchlorate | 9.8 |
| Laminac 4116/Lupersol | 6.8 |

Table 3. Small-scale performance of formulations **A** and **B** against the control.

| Formulation | Burn time [s] | Luminous intensity [cd] | Dominant wavelength [nm] | Spectral purity [%] |
|-------------|---------------|-------------------------|--------------------------|---------------------|
| Control | 32.2 | 423.5 | 623.0 | 86.4 |
| A | 39.4 | 544.3 | 620.6 | 89.1 |
| B | 35.6 | 812.8 | 618.2 | 90.6 |

Table 4. Prototype performance of formulations **A** and **B** against the perchlorate-containing control.

| Formulation | Burn time [s] | Luminous intensity [cd] | Dominant wavelength [nm] | Spectral purity [%] |
|-----------------------|---------------|-------------------------|--------------------------|---------------------|
| military requirements | 50.0 | 10000.0 | 620 ± 20 | 76.0 |
| control | 54.0 | 17194.9 | 613.1 | 88.6 |
| formulation A | 63.3 | 16285.0 | 612.5 | 89.9 |
| formulation B | 55.1 | 24490.1 | 612.7 | 91.6 |

board, with formulation **A** that burns 27 % longer and 72 % brighter, and with formulation **B** that burns 10 % longer and 150 % brighter (Table 4) than these specified values. Compared with the control, formulation **A** burned 17 % longer with comparable luminous intensity and formulation **B** burned for a comparable time with a luminosity increase of 42 %.

Although formulation **A** had a slightly lower luminous intensity than the control, it was a fair trade off given this formulation's remarkable burn time. Whereas luminous-intensity values normally decrease sharply with substantial increases in burn time, this was not the case with formulation **A**. Due to the comparable luminous intensity and superior burn time relative to the control, formulation **A** was determined to be a suitable candidate toward the development of a smaller and lighter HHS because less pyrotechnic material would be needed to achieve a burn time comparable to the control. Smaller and lighter HHSs would benefit military personnel by reducing their bulk load to be carried, thus enhancing maneuverability, survivability, and effectiveness on the battlefield.

Although the burn time of formulation **B** was comparable to the control, it is a sensible candidate for seeing a particular illuminant from a further distance due to the enhanced luminosity. Undoubtedly, the larger luminosity of formulation **B** was derived from the increased percentage of magnesium in the formulation,^[14] and this formulation can also be used as an HHS illuminant. Due to the large luminous intensity, formulation **B** (or a variant thereof) may be of commercial interest toward the development of environmentally friendly and brighter-burning red-light-emitting fireworks.

Although each illuminating candle was composed of approximately 90 g of pyrotechnic material consolidated in three equal increments at 3409 kg, epoxy-based formulations **A** and **B** were more dense than the Laminac-based control (Table 5). Because illuminant **A** burned 17 % longer than the control despite the 13 % shorter in size, it is feasible that illuminant **A** could be 30 % shorter than the control and still equal it in burn time with a comparable luminous intensity.

Table 5. Packing densities of formulations **A** and **B** and the perchlorate-containing control.

| Formulation | Height [cm] | Weight [g] |
|-------------|-------------|------------|
| control | 7.06 | 89.9 |
| A | 6.15 | 90.1 |
| B | 6.22 | 90.1 |

The sensitivities of formulations **A**, **B**, and the control toward various ignition stimuli are detailed in Table 6.^[15] Interestingly, formulations **A** and **B** had lower impact and friction sensitivities and a comparable thermal-onset temperature relative to the control. All formulations exhibited excellent resistance from ESD stimuli. The high stabilities of formulations **A** and **B** make these illuminants attractive candidates for production purposes and ensures that they are safe to handle and produce for possible military battlefield illuminating and civilian fireworks applications.

Table 6. Behavior of formulations **A** and **B** and the perchlorate-containing control toward various ignition stimuli.

| Formulation | Impact [J] | Friction [N] | ESD ^[a] [J] | Thermal onset [°C] |
|-------------|------------|--------------|------------------------|--------------------|
| control | 8.8 | 80 | >0.25 | 264.6 |
| A | 10.8 | 160 | >0.25 | 235.1 |
| B | 10.8 | >360 | >0.25 | 231.2 |

[a] ESD = electrostatic discharge.

Conclusion

In summary, perchlorate-free, red-light-emitting, HHS illuminants have been developed and proven out on the prototype at the production level. The high-nitrogen-containing illuminants disclosed are environmentally friendly, safer to handle than the control, free of the single-point-of-failure Laminac binder, and have exceptional performance. Once consolidated, formulation **A** was 13 % shorter in size, and burned 17 % longer with a comparable luminous intensity compared with the control. Formulation **A** is an excellent candidate for smaller HHS development because it has the potential to be 30 % shorter than the control and still yield comparable results.

Due to the acceptable burn time and exceptional luminous intensity, formulation **B** can also be used as an HHS illuminant capable of being viewed from a further distance. Due to the brighter-burning nature, formulation **B** (or a derivative of this formulation) may also be of interest to the commercial fireworks industry toward the development of environmentally friendly and brighter-burning red-light-emitting fireworks.

Now that formulations **A** and **B** have been proven out at the prototype level, they will be incorporated into an HHS, launched into the air, and the performances will be recorded ballistically as part of a systems demonstration. The results of the systems demonstration will be reported in due course.

Experimental Section

Mg 30/50 was purchased from Reade, Mg 50/100 was purchased from Magnesium Elektron, and KClO₄, Sr(NO₃)₂, and PVC were purchased from Hummel Croton. Strontium bis(1-methyl-5-nitriminotetrazolate) monohydrate (**1**) was synthesized in house (Picatinny Arsenal, NJ) by a

proprietary procedure. Laminac 4116 was purchased from Ashland Chemical. Lupersol was purchased from Norac. Epon 813 was purchased from Hexion Specialty Chemicals. Versamid 140 was purchased from Cognis. All tested formulations were encased in noncoated Kraft fiberboard tubes, obtained from Security Signals.

All chemicals used in formulation preparation were dried in the oven overnight at 60°C, and were weighed out according to the weight percentages in the formulations. A binder system (95 % Laminac 4116–5 % Lupersol/80 % Epon 813–20 % Versamid 140) was introduced into a Hobart air-mixing bowl and was vigorously mixed by hand with a wooden tongue depressor for 2 min. All fuels (magnesium, polyvinyl chloride, and, in the case of formulations **A** and **B**, **1**) were simultaneously added into the bowl, and the mixture was blended with the aid of a B-blade at 207 kPa for 10 min. The air was turned off and all oxidizers (strontium nitrate and, in the case of the control, potassium perchlorate) were added into the bowl, and the pyrotechnic mixture was blended for 10 min at 207 kPa. The air was turned off, the inside of the mixing bowl was scraped with the B-blade to remove the pyrotechnic material sticking to the sides of the bowl, and the mixture was again blended for 10 min at 207 kPa. The pyrotechnic mixture was poured from the air-mixer bowl to a large ceramic bowl. Laminac 4116/Lupersol-based formulations were dried in the oven overnight to ensure full curing, and Epon 813/Versamid 140-based formulations were dried in air for 2–3 h at ambient temperature to ensure partial curing before consolidation.

Each formulation was weighed out in three 30 g increments, and was pressed into noncoated Kraft fiberboard tubes (length of 8.13 cm; inner diameter of 4.93 cm) with the aid of a tooling die (inner diameter of 5.08 cm) and a manual hand press at a consolidation dead load of 3409 kg. Between 89.9–90.1 g of energetic material was used per candle, three candles were prepared for each formulation, and the candles were dried overnight in the oven at 60°C. After being conditioned in the oven, a thin layer of thermite-based igniter slurry in acetone was applied to the top of each candle. After the candles were dried in the oven at 60°C for 2 h to evaporate the acetone, they were ignited at ambient temperature and pressure with an electric match in the light tunnel with an energy source of 2 V.

Optical emissive properties of these formulations were characterized by using both a single-element, photopic, light detector and a 2048-element optical spectrometer. The light detector we used was manufactured by International Light and is composed of a SED033 silicon detector (33 mm² area silicon detector with quartz window) coupled to a photopic filter (Y-filter) and a field of view limited hood (H-hood). The current output of the detector was converted to voltage by using a DL Instruments 1211 transimpedance amplifier. Voltage output was collected and analyzed from the amplifier by using a NI-6115 National Instruments datacard and in-house-developed, Labview-based, data acquisition and analysis software.

The optical emissive spectrum of each sample was measured with a 2048-element Ocean Optics HR2000 spectrometer coupled to a 400-micron-core optical fiber. The dominant wavelength and spectral purity was measured based on the 1931 CIE method by using illuminant C as the white reference point. The spectrometer was calibrated with both an Hg–Ar light source (Ocean Optics HG-1 wavelength standard) and a calibrated tungsten light source (Ocean Optics LS-1-Cal). The average dominant wavelength and spectral purity based on the full burn of the sample was calculated.

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Great balls of eco-friendly fire: Perchlorate-free pyrotechnic formulations with red-light-emitting qualities for military and civilian firework interests have been developed. The environmentally friendly formulations are stable to various ignition stimuli and are capable of burning longer with intense light emission (see figure).



Energetic Materials

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